

## Organosulfates in cloud water above the Ozarks' isoprene source region

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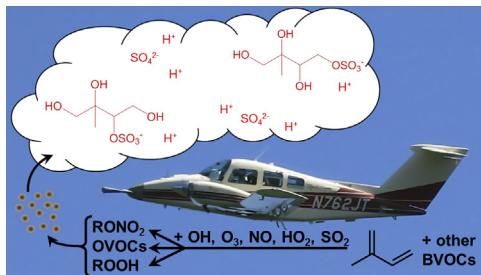
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### HIGHLIGHTS

- Organosulfates were detected in cloud water above the Missouri Ozarks.
- Biogenic volatile organic compound oxidation influenced the cloud chemistry.
- An organosulfate, derived from isoprene epoxydiols, was detected.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 14 December 2012

Received in revised form

2 May 2013

Accepted 4 May 2013

#### Keywords:

Isoprene

Cloud water

Organosulfate

CMAQ

### ABSTRACT

Secondary organic aerosol formation via aqueous processing, particularly from the oxidation of biogenic volatile organic compounds, is hypothesized to contribute significantly to the global aerosol burden. In this study, electrospray ionization coupled with mass spectrometry (ESI-MS) was utilized to detect organosulfates and oligomers in cloud water collected in July above the Missouri Ozarks, an environment significantly influenced by isoprene oxidation. Community Multiscale Air Quality (CMAQ) modeling suggested that the aerosol at cloud height was characterized by high water, sulfate, and biogenic secondary organic aerosol content, conducive to aqueous-phase processing and organosulfate formation. CMAQ modeling also suggested the presence of gas-phase organic peroxides and nitrates, which can partition into the particle-phase and form organosulfates. Several potential organosulfates from isoprene, monoterpene, and sesquiterpene oxidation were detected in the cloud water. In particular, the ubiquitous organosulfate  $C_5H_{12}O_7S$  (detected by ESI-MS at  $m/z = 215$ ), derived from isoprene epoxydiols, was detected. These results highlight the role of aqueous-phase reactions in biogenic SOA formation and cloud processes in isoprene oxidation-influenced regions.

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### 1. Introduction

Atmospheric aerosols influence visibility, the Earth's energy balance, and the hydrological cycle by scattering and absorbing radiation and acting as cloud condensation and ice nuclei (Pöschl, 2005). Organic species comprise a significant mass fraction of

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submicron aerosol particles with considerable contribution from secondary organic aerosol (SOA). SOA formation from biogenic volatile organic compounds (BVOCs), emitted primarily from forest ecosystems, is estimated to contribute greater than 50% of the total OA burden globally (Hallquist et al., 2009). Isoprene, with the highest emission rate ( $\sim 600 \text{ Tg C yr}^{-1}$ ) of all non-methane BVOCs, contributes significantly (estimated at  $\sim 27\text{--}78\%$ ) to global SOA concentrations (Carlton et al., 2009). Organic aerosol concentrations have been under-predicted by models with the magnitude of the bias peaking in the Northern Hemisphere in the spring/summer, suggesting contributions from BVOCs, wildfires, and/or photochemical activity (Heald et al., 2010). When the formation of low-volatility organics through aqueous-phase reactions was included for cloud droplets and aqueous particles, modeled predictions of organic carbon improved (Carlton et al., 2008).

Aumont et al. (2000) and Blando and Turpin (2000) suggested that cloud and fog processing could produce SOA, wherein organics absorbed into water droplets undergo chemical reactions, the products of which remain, in part, in the particle-phase upon droplet evaporation. In the laboratory, Altieri et al. (2006) observed oligomer formation in the photochemical aqueous reaction of pyruvic acid and hydrogen peroxide. Since then, numerous laboratory studies have been conducted, showing the formation of a variety of high molecular weight organic compounds within aqueous solutions (Ervens et al., 2011). Sorooshian et al. (2006) showed in-cloud production of oxalic acid through aircraft-based measurements and evaluation with a cloud parcel model. Most recently, Lee et al. (2011, 2012) showed increases in the oxygen content of dissolved organics upon aqueous OH oxidation of ambient SOA and cloud water samples collected at Whistler, British Columbia. However, despite the recent increase in studies of aqueous-phase reactions and evaluation of organic aerosol concentrations at surface locations characterized by high relative humidity (RH) (Ervens et al., 2011), few studies (Feng and Möller, 2004; Lee et al., 2012; Samy et al., 2010; van Pinxteren and Herrmann, 2007) have investigated the presence of high molecular weight compounds in cloud water.

Cloud processing of isoprene oxidation products alone is suggested to produce  $\sim 2 \text{ Tg SOA yr}^{-1}$  globally (4–20% of biogenic SOA production) (Lim et al., 2005), with more recent estimates of total global cloud SOA production being  $\sim 20\text{--}30 \text{ Tg yr}^{-1}$  (Liu et al., 2012). Therefore, to investigate the potential influence of biogenic SOA on clouds, cloud water was collected in July above the Missouri Ozarks, an environment that is heavily influenced by isoprene emissions ( $\sim 5 \text{ mg h}^{-1} \text{ m}^{-2}$ ) (Wiedinmyer et al., 2005). The Community Multiscale Air Quality (CMAQ) model was utilized to simulate BVOC oxidation products and SOA likely present at cloud height above the Ozarks. Electrospray ionization mass spectrometry (ESI-MS) was used to examine water-soluble organic compounds in the cloud water, and tandem mass spectrometry experiments targeted organosulfates, which are tracers of the reaction of aqueous-phase aerosol sulfate with BVOC oxidation products (Hoyle et al., 2011; McNeill et al., 2012). Laboratory studies have shown increased SOA yields, attributed to organosulfate formation, from BVOC oxidation in the presence of acidic seed aerosol (Surratt et al., 2007). Near the Ozarks in the summer, Tolocka and Turpin (2012) estimated high contributions of organosulfates to organic mass (up to  $\sim 25\%$ ). BVOC-derived organosulfates have previously been detected in ambient aerosol (e.g., Surratt et al., 2008), fogwater (LeClair et al., 2012), and rainwater (Altieri et al., 2009). Here, likely BVOC precursors to the observed organosulfates and oligomers in the cloud water are discussed.

## 2. Methods

### 2.1. Cloud water sampling and analysis

The middle/upper sections of developing (non-precipitating) cumulus clouds were sampled at  $\sim 2100 \text{ m}$  and  $\sim 2440 \text{ m}$  (above mean sea level) on July 13, 2007 at  $\sim 14:00$  local time above the Missouri Ozarks (38.15 N, 91.89 W). Using the method of Hill et al. (2007), cloud water samples (8 mL at each altitude) were collected using a modified Mohnen slotted rod cloud water collector (Huebert et al., 1988), which extended above the top of a Beechcraft Duchess twin-engine aircraft. Cloud droplets impacted onto the Teflon rods of the collector, characterized by a 50% cutoff diameter of  $\sim 5.5 \mu\text{m}$  (Kim and Boatman, 1992), and were collected in glass bottles. Samples were filtered (Restek, 0.22  $\mu\text{m}$  pore size, polyvinyl difluoride) to remove insoluble particles and stored at  $-20^\circ\text{C}$ . Organic carbon analysis was performed using a Shimadzu TOC-VCSH analyzer.

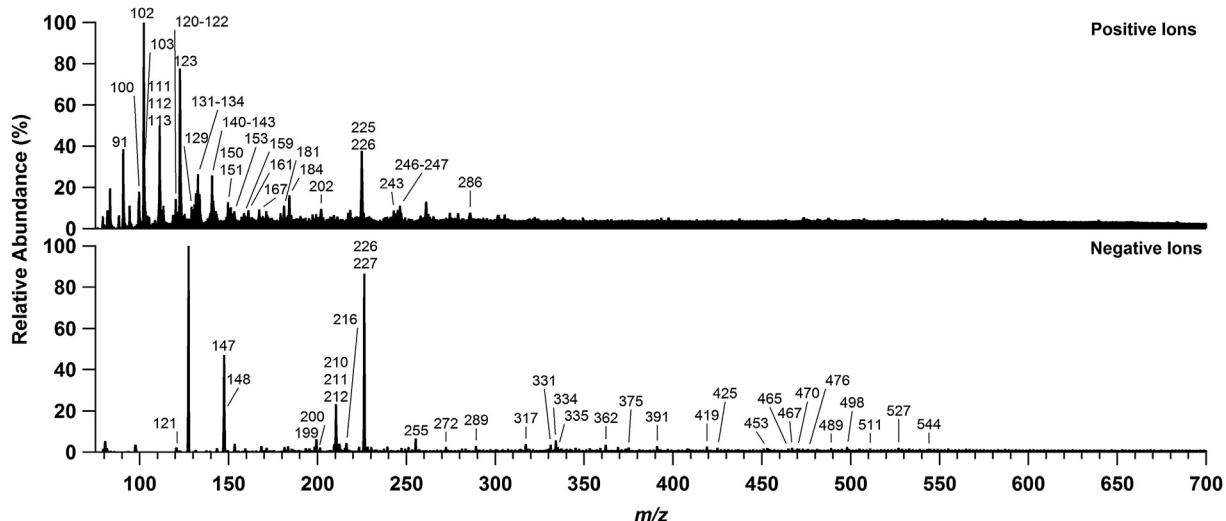
For ESI-MS, samples were concentrated using ultrapure nitrogen at room temperature and then diluted with 1:1 acetonitrile:water (v/v). ESI-MS was completed using a Thermo Finnigan IonMax source on a linear ion trap mass spectrometer. Both positive and negative ESI modes were employed, as described in the Supplementary Information. Unfortunately, the small volume of cloud water collected did not permit high-resolution mass spectrometric measurement following initial low resolution tandem mass spectrometry analysis. Organosulfates were identified through  $\text{MS}^2$  experiments through production of  $m/z -97 (\text{HSO}_4^-)$  or neutral loss of 80 Da ( $\text{SO}_3$ ) (Attygalle et al., 2001; Romero and Oehme, 2005; Surratt et al., 2007). Since only odd-numbered negative ion masses (from  $m/z 150\text{--}600$ ) were monitored during the  $\text{MS}^2$  experiments, any organosulfate compound containing an odd number of nitrate groups, for example, would not be identified. Due to the small sample volume, only the 80 Da neutral loss experiment was performed for the  $\sim 2440 \text{ m}$  cloud water sample. Based on a laboratory ESI-MS experiment using synthesized isoprene epoxydiol (IEPOX) and sodium sulfate, organosulfates were not expected to have formed within the ESI source, as discussed in the Supplementary Information and supported by previous studies (Romero and Oehme, 2005; Stone et al., 2009; Surratt et al., 2007).

### 2.2. Chemical transport modeling

The Community Multiscale Air Quality (CMAQ) model v4.7.1 ([www.cmaq-model.org](http://www.cmaq-model.org)), a 3D Eulerian one-atmosphere photochemical transport model (Carlton et al., 2010; Foley et al., 2010), was used to simulate July 1998, as described by Carlton and Baker (2011). CMAQ modeling of 1998, rather than 2007, was completed, as discussed in the Supplementary Information, due to the extensive previous comparisons of emission fluxes and trace gas concentrations with measurements in this region (Carlton and Baker, 2011; Wiedinmyer et al., 2005). The aerosol and gas-phase organic composition for all days in July 1998 at 14:00 local time and within the 12 km square sized grid cell containing the cloud sampling location at 2100 m was extracted for further analysis.

## 3. Results and discussion

For the cloud water samples collected at  $\sim 2100 \text{ m}$  and  $\sim 2440 \text{ m}$ , the dissolved organic carbon content was determined to be  $9.9 \text{ mg C L}^{-1}$  and  $6.5 \text{ mg C L}^{-1}$ , respectively, similar to previous cloud water studies (range of  $5\text{--}12 \text{ mg C L}^{-1}$ ) in a variety of locations (Hutchings et al., 2009). The dissolved organic content and chemical composition reported herein may at least partly reflect



**Fig. 1.** Positive and negative ion mass spectra for cloud water collected at ~2100 m. To highlight prominent ions, labels indicate positive ion peaks with relative abundances greater than 15% and intensities greater than 2\*control sample; negative ion peaks with intensities greater than 1.5\*control sample are also labeled.

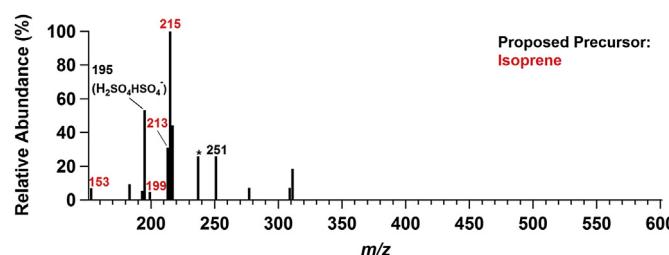
SOA produced following evaporation of cloud droplets, since the cloud water was first concentrated in the analysis procedure. Positive and negative ion mass spectra for cloud water collected at ~2100 m are shown in Fig. 1 for  $m/z$  75–700. To our knowledge, the mass spectra shown in Figs. 2, 3, and S3 represent the first observations of organosulfates in cloud water. The sulfate groups were likely characterized by primary or secondary functionality, which undergo hydrolysis less rapidly than tertiary sulfate groups (Darer et al., 2011). The second most abundantly observed precursor ion in Fig. 2 ( $m/z$  195), likely corresponds to sulfuric acid, detected as  $\text{H}_2\text{SO}_4\cdot\text{HSO}_4^-$ . While ESI-MS analyses generally use liquid chromatography to separate inorganic sulfate prior to ESI, this was not employed here; however, as discussed in the Supplementary Information, the observed organosulfates were not expected to be artifacts. The cloud water was likely acidic, given previous cloud water studies in the eastern U.S. ( $\text{pH} \sim 3.5$ ) (Straub et al., 2012) and an average observed pH of 6.0 for rainwater collected in July 2007 at the National Atmospheric Deposition Program monitoring site, ~72 km north of the cloud water sampling location.

In the CMAQ simulations, the average  $\text{PM}_{2.5}$  mass concentration at ~2100 m was simulated to be  $3.0 (\pm 0.7) \mu\text{g m}^{-3}$  with  $32 (\pm 6)\%$  of the  $\text{PM}_{2.5}$  mass as water, highlighting the potential for aqueous-phase processing. Reported uncertainties indicate variability of the predictions within the modeled month at 14:00 local time, rather than the uncertainties in the simulated mechanisms (Carlton et al., 2010). The simulated average  $\text{PM}_{2.5}$  mass, not including water,

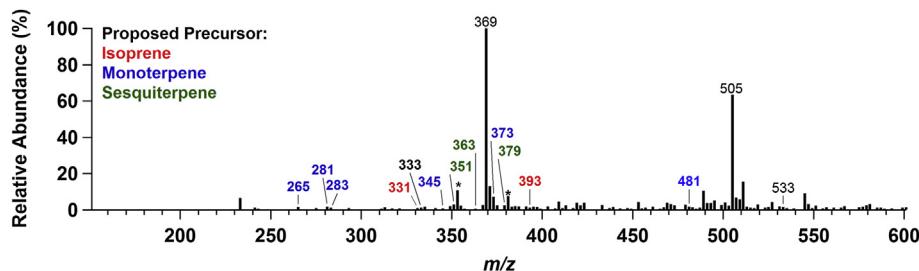
was  $50 (\pm 5)\%$  sulfate,  $20 (\pm 3)\%$  organic,  $16 (\pm 1)\%$  ammonium,  $1.1 (\pm 0.6)\%$  nitrate, and  $14 (\pm 2)\%$  other species. Of the total organic aerosol mass,  $69 (\pm 5)\%$  was estimated to be SOA, of which up to  $79 (\pm 4)\%$  was estimated to originate from BVOC precursors (Fig. 4). Significantly, biogenic oligomer SOA, formed via particle-phase reactions of oxidation products of isoprene, monoterpene, and sesquiterpenes, comprised  $55 (\pm 7)\%$  of the simulated SOA (Fig. 4), indicating the likely presence of high molecular weight organic species. The cloud water mass spectra (Fig. 1) show an abundance of species at less than ~300 Da. This is consistent with previous isoprene SOA studies showing decomposition of oligomers at high RH and in aqueous solution (Nguyen et al., 2012a, 2011; Zhang et al., 2012; Zhang et al., 2011). However, direct comparison of ambient mass spectra with laboratory studies is difficult due to the complexity of SOA precursors and reaction pathways in the atmosphere. Therefore, molecular tracers, including organosulfates, can be used to probe the influence of biogenic VOC oxidation (Hoyle et al., 2011). Given the high relative aerosol water, sulfate, and biogenic SOA simulated mass fractions, the presence of particle-phase organosulfates from BVOC precursors is expected (Darer et al., 2011; McNeill et al., 2012; Zhang et al., 2011), while not explicitly included in the CMAQ model. In Sections 3.1 and 3.2, we discuss potential biogenic SOA tracers, focusing on organosulfates, observed in the cloud water.

### 3.1. Isoprene oxidation

Semivolatile isoprene oxidation products were simulated to be  $0.19 (\pm 0.08)$  ppb on average at cloud height (Fig. S4). Correspondingly, SOA derived primarily from gas-particle partitioning of isoprene oxidation products contributed  $6 (\pm 2)\%$  on average to the CMAQ simulated SOA at cloud height with additional contributions from particle-phase reactions, producing biogenic oligomer SOA (Fig. 4). Isoprene SOA contributions were likely even greater than simulated due to recently identified formation pathways via IEPOX (Surratt et al., 2010) and methacrylic acid epoxide (MAE) (Lin et al., 2013), not included in the CMAQ model. In the mass spectral analysis of the cloud water, we first concentrate on probable markers of isoprene oxidation observed. Characterized by loss of  $\text{HSO}_4^-$ ,  $m/z$  215 likely corresponds to  $\text{C}_5\text{H}_{11}\text{O}_7\text{S}^-$  (Fig. 2), a sulfate ester produced via reactive uptake of IEPOX, formed from isoprene



**Fig. 2.** Negative ion mass spectrum of precursor ions corresponding to loss of  $m/z$  -97 ( $\text{HSO}_4^-$ ), characteristic of organosulfates, for cloud water collected at ~2100 m. Peaks labeled in red correspond to species with isoprene as the proposed precursor. \*Ion peak observed in control sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Negative ion mass spectrum of precursor ions corresponding to neutral loss of 80 Da ( $\text{SO}_3$ ), characteristic of organosulfates, for cloud water collected at ~2100 m. Peaks labeled in red, blue, or green correspond to species with isoprene, monoterpenes, or sesquiterpenes, respectively, as the proposed precursors. \*Ion peaks, at >5% relative abundance, observed in control sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

photooxidation under low- $\text{NO}_x$  conditions (e.g., Surratt et al., 2007). During laboratory studies, the abundance of this organosulfate increased with sulfate seed acidity (Surratt et al., 2007), as well as RH (Zhang et al., 2011). Modeling suggests that this IEPOX-derived organosulfate comprises the majority of organosulfate mass under low- $\text{NO}_x$  aqueous-aerosol conditions (McNeill et al., 2012). This isoprene-derived organosulfate has been observed in numerous measurements of ambient aerosol (Chan et al., 2010; Froyd et al., 2010; Gómez-González et al., 2008, 2012; Hatch et al., 2011; Kristensen and Glasius, 2011; Stone et al., 2012; Surratt et al., 2008, 2007; Worton et al., 2011; Yttri et al., 2011; Zhang et al., 2012).

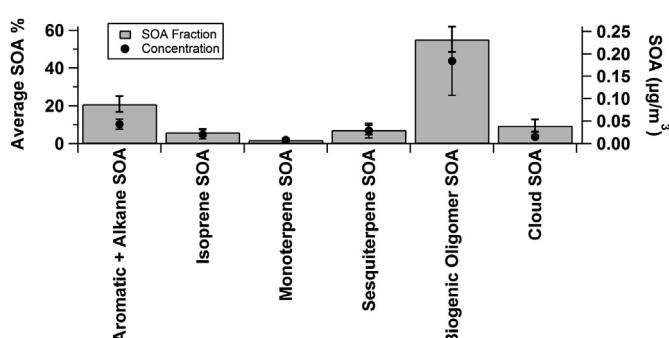
In the laboratory, the  $m/z - 215$  organosulfate has been shown to form via aqueous reaction of isoprene with  $\text{SO}_4$  radicals (Nozière et al., 2010). However, the average CMAQ simulated mixing ratios of primary BVOCs (isoprene, monoterpenes, and sesquiterpenes) were very low (26 ppt, 0.5 ppt, and <0.01 ppt, respectively) compared to their oxidation products (Fig. S4), which formed during transport to cloud height. As noted in the Supplementary Information, only marginal atmospheric instability was present during sampling, further suggesting that the cloud water was primarily impacted by biogenic VOC oxidation products, rather than their primary precursors. Further, aqueous SOA precursors must be water-soluble, with Henry's Law coefficients of greater than  $\sim 10^3 \text{ M atm}^{-1}$  (Gelencsér and Varga, 2005), to form SOA via cloud processing, such that any contribution from primary BVOCs would be minimal; this further suggests oxidation products, such as IEPOX, as aqueous SOA precursors.

Other possible isoprene-derived organosulfate ions, identified by loss of  $\text{HSO}_4^-$ , include (in order of ion abundance):  $m/z - 213$ ,

–251, –153, and –199 (Fig. 2, Table S1). Previously, low- $\text{NO}_x$  isoprene photooxidation chamber studies in the presence of acidic aerosol seed resulted in SOA characterized by  $m/z - 213$ , assigned to  $\text{C}_5\text{H}_9\text{O}_7\text{S}^-$  (Surratt et al., 2008). This isoprene-derived organosulfate has been detected in ambient aerosols (Gómez-González et al., 2008; Kristensen and Glasius, 2011; Surratt et al., 2008), as well as rainwater (Altieri et al., 2009). An organosulfate at  $m/z - 251$  has previously been identified as  $\text{C}_8\text{H}_{11}\text{O}_7\text{S}^-$  from the reaction of methyl vinyl ketone with  $\text{SO}_4$  radicals in aqueous solution (Nozière et al., 2010). Hydroxyacetone, a product of high- $\text{NO}_x$  isoprene photooxidation, has been identified previously as a precursor to an organosulfate at  $m/z - 153$  ( $\text{C}_3\text{H}_5\text{O}_5\text{S}^-$ ) (Surratt et al., 2008, 2007), which has been observed previously in ambient aerosol (Froyd et al., 2010; Hatch et al., 2011; Surratt et al., 2008) and rainwater (Altieri et al., 2009). An organosulfate at  $m/z - 199$  ( $\text{C}_4\text{H}_7\text{O}_7\text{S}^-$ ) has been observed in studies of high- $\text{NO}_x$  isoprene photooxidation (Surratt et al., 2008, 2007), high- $\text{NO}_x$  methacryloylperoxynitrate photooxidation (Surratt et al., 2010), and high- $\text{NO}_x$  methacrolein photooxidation (Zhang et al., 2012). Recently, Lin et al. (2013) found that this organosulfate is directly derived from reactive uptake of gaseous MAE, which is produced from the reaction of methacryloylperoxynitrate with OH, onto acidic sulfate aerosols. The reactions of both methyl vinyl ketone and methacrolein with  $\text{SO}_4$  radicals in aqueous solution have also produced an organosulfate with this molecular ion (Nozière et al., 2010). An organosulfate at  $m/z - 199$  has been observed in ambient aerosol in the southeastern U.S. (Hatch et al., 2011; Surratt et al., 2008; Zhang et al., 2012). In recent studies of methacrolein photooxidation, organosulfates observed at  $m/z - 153$  and –199 were more abundant under wet conditions (RH >30%) compared to dry conditions (RH <20%) (Zhang et al., 2012).

Additional organosulfates, possibly derived from isoprene, were observed by neutral loss of  $\text{SO}_3$  for the cloud water samples collected at 2100 m and 2440 m (Figs. 3 and S3, Table S2). Organosulfates at  $m/z - 331$  and –333 have been observed during low- $\text{NO}_x$  isoprene photooxidation experiments (Surratt et al., 2010, 2008, 2007). An ion at  $m/z - 333$ , attributed to the hydroxyl sulfate ester dimer of the IEPOX organosulfate ( $m/z - 215$ , Fig. 2) (Surratt et al., 2010), has been detected previously in ambient aerosol (Froyd et al., 2010; Surratt et al., 2008). An ion at  $m/z - 393$  has previously been suggested as an organosulfate tetramer of methyl vinyl ketone ( $\text{C}_{16}\text{H}_{25}\text{O}_9\text{S}^-$ ) from aqueous sulfate radical oxidation reactions (Nozière et al., 2010).

Many of the negative ions ( $\text{M}-\text{H}^-$ ) observed for the 2100 m cloud water sample (Fig. 1) correspond to masses detected by Nguyen et al. (2011) in SOA produced from high- $\text{NO}_x$  isoprene photooxidation at high RH (90%). Several of the abundant high mass ions observed during the cloud water analysis ( $m/z - 289$ , –335, –391, –425, –453, –467, –470, –511, and –527), may correspond to oligomers of 2-methylglyceric acid ( $\text{C}_4\text{H}_8\text{O}_4$ )



**Fig. 4.** Average CMAQ simulated July (14:00 local time) concentrations and fractions of SOA types for the cloud sampling location. Aromatic + alkane SOA, also includes oligomers formed from particle-phase reactions from these oxidation products. Biogenic oligomer SOA was defined as being formed from particle-phase reactions of biogenic VOC oxidation products. Cloud SOA was defined as being formed from in-cloud OH oxidation of glyoxal and methylglyoxal (Carlton et al., 2008). Uncertainty bars indicate the variability (95% confidence intervals) over the simulated month at 14:00 local time.

(Nguyen et al., 2011; Surratt et al., 2006; Zhang et al., 2012). 2-methylglyceric acid is formed from the uptake and subsequent hydrolysis of MAE on acidic sulfate aerosol (Lin et al., 2013); MAE is also suggested as a possible precursor to the  $m/z$  –199 organosulfate (Fig. 2), discussed above.

CMAQ modeling suggested that 10 ( $\pm 3\%$ ) of the total simulated SOA at the cloud height of 2100 m was from in-cloud OH oxidation of glyoxal and methylglyoxal (Fig. 4), both of which are water-soluble isoprene oxidation products (Carlton et al., 2009). For the sampled cloud water, several observed ion peaks (Fig. 1) could correspond to reaction products of these precursors. In the study of glyoxal uptake on ammonium sulfate aerosol, Galloway et al. (2009) detected the formation of  $m/z$  129 ( $C_5H_9N_2O_2^+$ ), 159 ( $C_6H_{11}N_2O_3^+$ ), and 184 ( $C_7H_{10}N_3O_3^+$ ). Aqueous OH oxidation of glyoxal has shown to produce  $m/z$  –121 ( $C_3H_5O_5^-$ ) and –147 ( $C_4H_3O_6^-$ ) (Lim et al., 2010).  $m/z$  91 (Fig. 1) could be attributed to methylglyoxal, in its protonated geminal-diol form ( $C_3H_7O_3^+$ ) (Yasmeen et al., 2010). Previously, atomized aqueous solutions of acetaldehyde, methylglyoxal, and ammonium sulfate resulted in formation of  $m/z$  121 and 129, assigned in those studies as  $C_5H_{11}O_3^+$  and  $C_6H_7O_3^+$ , respectively (Li et al., 2011).

Laboratory studies show many additional possible precursors and mechanisms of aqueous SOA formation (Ervens et al., 2011), which suggests that the contributions of aqueous SOA formation could be greater than simulated by the CMAQ model. Since isoprene SOA and isoprene oxidation products were predicted by CMAQ to be in significant concentrations at cloud height (Figs. 4 and S4), the mass spectra (Fig. 1) were examined for additional potential markers of aqueous processing. In the aqueous photooxidation of the water-soluble isoprene oxidation product glycolaldehyde ( $C_2H_4O_2$ ),  $m/z$  –147 and –289 were observed and assigned as glycolic acid oligomers ( $C_5H_7O_5^-$  and  $C_{11}H_{13}O_9^-$ , respectively) (Perri et al., 2009); however, glycolic acid sulfate ( $m/z$  –155) (Olson et al., 2011) was not observed in the cloud water MS<sup>2</sup> organosulfate experiments, suggesting that a different ion assignment may be possible. Ions potentially corresponding to oligomers of glycolaldehyde, observed during isoprene photooxidation SOA studies (Nguyen et al., 2011), included  $m/z$  –335 ( $[C_5H_7O_4 + (C_4H_6O_3)_2]^-$ ), –453 ( $[C_5H_7O_5 + (C_4H_6O_3)_3]^-$ ), and –425 ( $[C_8H_9O_5 + (C_2H_4O_2)_4]^-$ ). In the aqueous photooxidation of the isoprene oxidation product pyruvic acid, Altieri et al. (2006) observed  $m/z$  –147, formed from pyruvic and acetic acids, to be one of the most abundant ions produced after 10 min of reaction. Ions at  $m/z$  –147 and –453 (Fig. 1) have also been attributed to mono-formate oligomers during high-NO<sub>x</sub> isoprene photooxidation experiments (Nguyen et al., 2011; Surratt et al., 2006; Zhang et al., 2012).

Gas-phase organic nitrates were predicted by CMAQ to be abundant at cloud height (Fig. S4). Hydroxy alkyl nitrates, which form in the gas-phase from reaction with NO<sub>3</sub> or via consecutive additions of OH, O<sub>2</sub>, and NO, have significant Henry's Law coefficients ( $\sim 10^4$ – $10^5$  M atm<sup>-1</sup>) (Shepson et al., 1996), making them excellent candidates as aqueous SOA precursors. Once in the aqueous phase, tertiary organonitrates quickly undergo nucleophilic substitution reactions with sulfate, forming organosulfates, or undergo hydrolysis to form polyols (Darer et al., 2011). For the cloud water samples, several ions (Fig. 1) potentially correspond to organonitrates and related compounds. Previous high-NO<sub>x</sub> isoprene, methacrolein, and MPAN photooxidation studies have shown the formation of an organonitrate at  $m/z$  –470 ( $C_{16}H_{24}NO_{15}$ ), as well as a corresponding polyol at  $m/z$  –425 ( $C_{16}H_{25}O_{13}$ ) that results from hydrolysis of the tertiary organonitrate (Surratt et al., 2010, 2006). Likewise, if  $m/z$  –498 (Fig. 1) was the isoprene-derived organonitrate  $C_{17}H_{25}O_{16}N$  (Nguyen et al., 2011), the corresponding organosulfate could be  $m/z$  –533 (Fig. 3). Similarly, the

abundant organosulfate ion at  $m/z$  –369 (Fig. 3), with an unknown precursor, could be related to the ion at  $m/z$  –334 (Fig. 1).

### 3.2. Monoterpene and sesquiterpene oxidation

Semivolatile monoterpene and sesquiterpene oxidation products are predicted by the CMAQ model to be at lower mixing ratios ( $70 \pm 20$  ppt and  $18 \pm 8$  ppt, respectively) than semivolatile isoprene oxidation products (Fig. S4). SOA derived primarily from gas-particle partitioning of monoterpene and sesquiterpene oxidation products contributed 1.9 ( $\pm 0.5\%$ ) and 7 ( $\pm 3\%$ ), respectively, on average to the afternoon SOA over the simulated month; particle-phase reactions of these species also produced biogenic oligomer SOA (Fig. 4). For the cloud water, several organosulfates can potentially be attributed to monoterpene and sesquiterpene oxidation. An organosulfate at  $m/z$  –265 (Fig. 3, Table S2) was previously observed in SOA in the southeastern U.S. (Surratt et al., 2007). In the high-NO<sub>x</sub> photooxidation of  $\alpha$ -pinene in the presence of SO<sub>2</sub>, as well as acidic aerosol, Surratt et al. (2008, 2007) assigned  $m/z$  –265 to  $C_{10}H_{17}O_6S^-$  with pinonaldehyde as the proposed precursor (Liggio and Li, 2006). High-NO<sub>x</sub> photooxidation of  $\alpha$ -terpinene and terpinolene in the presence of acidic aerosol also produces organosulfates at  $m/z$  –265 (Surratt et al., 2008). Organosulfates at  $m/z$  –281 and –283 (Figs. 3 and S3) have been detected together previously in ambient aerosol (Mazzoleni et al., 2012; Surratt et al., 2008) and rainwater (Altieri et al., 2009). Laboratory studies of the reaction of sulfate radicals with  $\alpha$ -pinene in aqueous solution have shown production of  $C_{10}H_{17}O_7S^-$  and  $C_{10}H_{19}O_7S^-$  ( $m/z$  –281 and –283, respectively) (Nozière et al., 2010); however, it is important to note that primary BVOCs were unlikely aqueous precursors, as discussed in section 3.1. Formation of a  $m/z$  –281 organosulfate has also been observed during photooxidation experiments of  $\alpha$ -pinene, limonene,  $\alpha$ -terpinene, terpinolene, and  $\beta$ -pinene, as well as the ozonolysis of limonene, in the presence of acidic aerosol, generally under high-NO<sub>x</sub> conditions (Iinuma et al., 2007b; Surratt et al., 2008). Similarly, organosulfates at  $m/z$  –283 have been observed during high-NO<sub>x</sub> monoterpene ( $\alpha$ -terpinene, terpinolene, and  $\beta$ -pinene) photooxidation experiments in the presence of acidic aerosol (Surratt et al., 2008).

For the 2100 m and 2440 m cloud water samples (Figs. 3 and S3), a  $m/z$  –345 organosulfate has been previously observed as  $C_{10}H_{18}S_2O_9^-$  after uptake of pinonaldehyde, an oxidation product of  $\alpha$ -pinene, on sulfate aerosol (Liggio and Li, 2006). The high-NO<sub>x</sub> photooxidation of monoterpenes containing more than one carbon–carbon double bond (e.g., limonene,  $\beta$ -phellandrene,  $\alpha$ -terpinene, terpinolene) has been shown to produce an organosulfate with two nitrate groups at  $m/z$  –373 ( $C_{10}H_{17}N_2O_{11}S^-$ ) (Surratt et al., 2008). This organosulfate was observed in ambient aerosol collected in forested areas (Iinuma et al., 2007a; Kristensen and Glasius, 2011). In addition to contributions from isoprene oxidation, noted in section 3.1, an organosulfate at  $m/z$  –251 (Fig. 2) has also been observed in monoterpene photooxidation studies (Chan et al., 2011; Surratt et al., 2008). High-NO<sub>x</sub>  $\beta$ -caryophyllene photooxidation experiments have also shown organosulfates at  $m/z$  –333, –351, –363, and –379 (Figs. 3 and S3) (Chan et al., 2011). Additionally, an organosulfate at  $m/z$  –481 ( $C_{20}H_{33}O_{11}S^-$ ) has been observed in the ozonolysis of limonene in the presence of acidic seed aerosol (Iinuma et al., 2007b).

Several ions in Fig. 1 can also be potentially assigned to monoterpene and sesquiterpene oxidation products. For example, in addition to likely contributions from isoprene oxidation products,  $m/z$  –199 may also correspond to deprotonated hydroxypinonic acid, one of the most abundant SOA products from  $\alpha$ -pinene ozonolysis (Iinuma et al., 2004). Similarly, deprotonated  $\beta$ -hydroxy-nornocaryophyllonic acid (previously observed at  $m/z$  –255) and

its dimer ( $m/z -511$ ) have been observed as products of high- $\text{NO}_x$   $\beta$ -caryophyllene oxidation, which potentially produced some of the observed organosulfates, discussed above (Chan et al., 2011). Ions at  $m/z$  111, 113, and 143 have been previously detected in terpinolene oxidation studies as  $\text{C}_6\text{H}_{11}\text{O}^+$ ,  $\text{C}_6\text{H}_9\text{O}_2^+$ , and  $\text{C}_7\text{H}_{11}\text{O}_3^+$ , respectively (Lee et al., 2006).

#### 4. Conclusions

Aqueous processing of isoprene oxidation products has been predicted as a significant global source of SOA (Lim et al., 2005). Cloud water collected above the Missouri Ozarks, a region influenced by isoprene emissions and oxidation, revealed the presence of organosulfates. This finding was consistent with CMAQ modeling, which predicted the presence of gas-phase organic peroxides and nitrates, as well as aerosol characterized by significant water, sulfate, and biogenic SOA mass fractions. Many of the prominent organosulfates and high mass species observed in the cloud water were consistent with SOA formed from gas-particle partitioning of isoprene photooxidation products and corresponding particle-phase reactions, observed in previous laboratory studies. Based on reaction time scales, Ervens et al. (2011) hypothesized that aqueous processing within atmospheric particles has a greater contribution to SOA formation than cloud processing. In particular, organosulfates are suggested to be tracers of aqueous aerosol-phase chemistry rather than cloud processing, since modeling has shown maximum formation under low RH, acidic conditions (McNeill et al., 2012). Since cloud water chemistry reflects multiple cycles of cloud processing and evaporation (Nguyen et al., 2012b), the lack of highly-abundant oligomers greater than  $\sim 300$  Da (Fig. 1) may highlight the importance of fragmentation reactions in aqueous processing (Nguyen et al., 2012a). Overall, the oxidation products of isoprene, several monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene,  $\alpha$ -terpinene, terpinolene, limonene,  $\beta$ -phellandrene), and  $\beta$ -caryophyllene were hypothesized as BVOC precursors to the observed organosulfates. However, the only sesquiterpene studied in the laboratory thus far with respect to organosulfate formation is  $\beta$ -caryophyllene (Chan et al., 2011). This suggests that other sesquiterpenes, predicted by CMAQ modeling to contribute significantly to the SOA mass loading at this location (Fig. 4), may have also contributed to the organosulfates, particularly the unknown higher mass organosulfates measured in the cloud water (Fig. 3 and S3). Future laboratory studies should focus on organosulfate formation from sesquiterpene oxidation.

The cloud water collected above the Missouri Ozarks highlights the role of biogenic SOA in aqueous-phase processes in this region. Given the presence of organosulfates in the cloud water, the biogenic SOA was likely internally mixed with particle-phase sulfate (Froyd et al., 2010; Hatch et al., 2011), which contributes to the cloud condensation nucleation efficiency of the individual particles (King et al., 2010). The simulated abundance of hydroperoxides and aldehydes at cloud height suggests that future aqueous-phase laboratory studies should investigate these species, as discussed in the Supplementary Information. Gas-particle partitioning of tertiary organic nitrates, produced in the gas-phase under high- $\text{NO}_x$  conditions, and subsequent hydrolysis and organosulfate production (Darer et al., 2011) may have a significant impact on SOA production, suggesting that future laboratory efforts should be focused on study of this pathway, which also has implications on the  $\text{NO}_x$  budget. Overall, aqueous SOA formation is likely significant in regions of high BVOC influence, relative humidity,  $\text{NO}_x$ , and sulfate aerosol content. These characteristics are often present in the southeastern U.S., where SOA formation from interactions of BVOC and anthropogenic emissions can form a significant and climate-relevant cooling haze (Goldstein et al., 2009).

#### Acknowledgments

Funding was provided by EPA STAR grants (G2007-STAR-E1 and 83504101). As the manuscript has not been formally reviewed by the EPA, the views expressed are solely those of the authors; the EPA does not endorse any products mentioned herein. K.A. Pratt acknowledges a NOAA Climate & Global Change Postdoctoral Fellowship, administered by the University Corporation for Atmospheric Research. J.D. Surratt was supported in part by the Electric Power Research Institute (EPRI). We thank A. Gold and Z. Zhang (Univ. of North Carolina at Chapel Hill) for IEPOX synthesis. R. Graham Cooks (Purdue Univ.) is thanked for discussions. Fatkhulla Tadzhimukhamedov (Purdue Univ.) and Kirk Baker (EPA) are thanked for instrumental and CMAQ model assistance, respectively.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2013.05.011>.

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